HIGH-STRENGTH PORTLAND CEMENT CONCRETE CONTAINING MUNICIPAL SOLID WASTE INCINERATOR ASH

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ABSTRACT

A variety of methods are being examined by numerous organizations to render hazardous solid residues non-hazardous and to create beneficial uses for ash from municipal solid waste incinerators. One method for both purposes is the replacement of a portion of the fine aggregate in Portland cement concrete. The strength of the concrete drops significantly as the portion replaced increases, even with normal additives. This paper presents the greatly improved strengths obtained with ash, which has been exposed to a new additive. These results show that up to 35% of the concrete can be made up of ash, while still obtaining compressive strengths of over 5000 psi (34.5 MPa). Micrographs of the original ash, ash and additive, concrete with ash but without additive, and concrete with ash and additive indicate the role of the additive. TCLP extractions of this novel new concrete have yet to be conducted. The economics, commercialization and extension of the development to other situations are discussed.

INTRODUCTION

As landfill space becomes more limited, it becomes more attractive to reduce the volume of materials being disposed there. Recycling is one approach, waste minimization is a second method, and combustion for energy production is the third, and ultimate, one. Ash from municipal solid waste (MSW) combustors can have less than 10% of the original volume entering the facility. A further reduction in landfilling, though, can be realized by developing a beneficial use for the ash. The most commonly considered beneficial use of ash is as an aggregate in either bituminous or Portland cement concrete. This method has the further advantage of displacing sand and gravel, which must be mined from sometimes environmentally sensitive locations. Another short-term advantage of this method is its ability to bind the toxic metals, entering with the MSW [1], into the concreted mass. Controversy over the long-term implication of the presence of these metals in the concrete has arisen, however. The Environmental Defense Fund has expressed vigorous concern for the long-term release of these metals as the concrete eventually degrades or is reduced to rubble [2].

Utilizing MSW incinerator ash in Portland cement concrete has been investigated by several organizations. At a number of locations, bottom ash (slag) from high-temperature combustors is utilized as coarse aggregate in regular concrete (see for example References 3 and 4). Utilization of low-strength concretes containing either

fly ash or mixed fly and bottom ash (combined ash) are moving toward commercial use in three directions.

One of these directions is to make block secondary products, such as artificial reef blocks, construction blocks, and shore protection devices [5]. Artificial reef blocks consist of 85% combined ash and 15% Portland (Type II) cement and have compressive strengths of about 1000 psi (6.9 MPa). By comparison, standard precast Portland cement concrete contains 40% coarse aggregate, 40% fine aggregate and 20% Portland cement and has a compressive strength of over 3500 psi (24.2 MPa). Construction blocks consist of 35-60% combined ash, 25-50% sand, 15% Portland (Type IP) cement, and sufficient Acme-Hardesty superplasicizer to allow the mix to flow easily. Compressive strengths vary from 1600 psi (11.0 MPa) to 2600 psi (17.9 MPa). A boathouse, built recently at the State University of New York at Stony Brook from 14,000 such construction blocks, is being evaluated for structural and environmental acceptability. Finally, shore protection devices require the use of a patented admixture, Chloranan (manufactured by Hazcon, Inc., of Brookshire, Texas) at a ratio of cement to admixture of 10:1. Using cement percentages between 17 and 33, compressive strengths up to 4200 psi (29.0 MPa) are reported.

A second approach is the accretion of combined ash with Portland cement (8-14%) into coarse aggregate for use in roadbeds and concrete [6]. This level of concretization provides aggregate with strengths of about 1200 psi (8.3 MPa), similar to the material, described in Reference 5. Finally, a third approach is the stabilization of combined ash with Portland cement (6-10%) to create land fill covers [7]. In all of these approaches, the ability of Portland cement concrete to reduce the leachability of trace metals from the concreted mass to meet TCLP standards has been a key element of their development.

A major area which these projects do not address is the precast concrete market. For entrance into this arena, compressive strengths between 3500 psi (24.2 MPa) and 5500 psi (38.0 MPa) must be achieved. In addition, extensive physical testing must be applied and minumum standards met. These tests include tensile strength, freeze-thaw, deicing, and abrasion. As the preceding brief review shows, obtaining the compressive strengths required by precasters has proven impossible with significant amounts of combined ash, even with standard additives. Only those concretes made with the addition of large amounts of Chloranan enter this range.

The School of Engineering at the University of Pittsburgh has recently discovered an inexpensive method which permits high-strength concrete to be produced, containing large amounts of combined ash from a MSW combustor. The method, which has just been disclosed to the University as the first step in the patent process, will now be described as thoroughly as possible within the limits imposed by that process.

PORTLAND CEMENT CONCRETE MANUFACTURE

In October 1988 the University of Pittsburgh began to study the utilization of MSW combustor ash in Portland cement concrete. Four 750-lb (1650-kg) samples of ash have been obtained during the past two years from the MSW combustor at Poughkeepsie, New York, operated for the Dutchess County Resource Recovery Agency by Dutchess Resource Energy, a subsidiary of the Resource Energy Systems

Division of Westinghouse Electric Corporation. The primary combustor in this facility is an O'Conner water-wall rotary kiln. The bottom ash drops into a water-filled pit, from which it is reclaimed past a grizzly to take out large particles, and a magnet for iron removal. The hot gases from the primary combustor pass through a secondary combustor, a boiler, and a dry scrubber. The fly ash and spent limestone (injected in the scrubber for acid gas removal) are added to the bottom ash just before the combined ash is loaded into trailers for hauling to a land disposal site.

The first two samples of ash were composited from 5-pound (11-kg) sub-samples of combined ash, collected six times daily for 25 days. Ash Sample #1, combined ash collected from mid-July to early September 1989, contained 8-21% moisture, 15.1% calcium oxide, 2.21% sulfur trioxide and 7.2% iron oxide and exhibited a 7.26% loss of ignition. Ash Sample #2 was bottom ash collected during January 1990. Ash Samples #3 and #4 were bottom ash collected in essentially one quick draw on May 24-25, 1990, and March 1-2, 1991, respectively. Ash Sample #3 contained 11.9% calcium oxide, 2.58% sulfur trioxide and 9.8% iron oxide and exhibited a 8.04% loss of ignition.

Six batches of concrete were made with Ash Sample #1 and fifteen batches with Ash Sample #2. The basic recipe was 17% coarse aggregate, 40% ash and 43% Portland cement. An air entrainment additiive, a water reduction additive and a silica fume additive were all tried individually with certain of these batches. The slump of each batch was held as close as possible to 1.75 inches (4.45 cm) by varying the water content. Concrete batches were produced in a small commercial mixer in the Concrete Laboratory of the Civil Engineering Department, following standard procedures. A number of cylinders (3 inches (7.6 cm) in diameter and 6 inches (15.2 cm) long) were formed from each batch. Cylinders were stored in an environmentally controlled room. Compressive strengths were measured on a Baldwin hydraulic compression tester, also located in the Concrete Laboratory of the Civil Engineering Department. Sets of four cylinders were cracked, and the load at breaking were averaged to obtain reported values of compressive strength.

Compressive strengths were generally in the range of 1000 psi (6.9 MPa) to 2300 psi (15.9 MPa). The ash in the first six batches of concrete were subjected to the Standard Extraction Procedure Method (the EP TOX procedure). The extractions were performed in the Environmental Laboratory of the Civil Engineering Department and leachates were sent to a commercial laboratory for analysis. Neither the ashes nor the concretes exceeded the EP TOX limits for any constituent. However, the ash and one of the six concrete batches (which happened to contain a lower amount of Portland cement a higher amount of coarse aggregate than according to the usual recipe, and which also contained some sand) exceeded the NYCRR limits for cadmium and lead. The presence of fly ash in Ash Sample #1 appeared to cause a number of "popouts". A white crystalline material, identified as a physical assemblage of aluminum chloride and calcium oxide crystals, was found at the focal point of all the popouts examined.

As Ash Sample #2 was running out, it was decided to attempt to modify the chemical and/or physical makeup of the surface of the ash particles to increase the strength of the bond between the ash and the cement. Two different commonly available chemicals were tried as additives in the last two batches of concrete made from Ash Sample #2. One of these novel additives did, in fact, yield compressive

strengths of nearly 4000 psi (36.0 MPa). Therefore, a set of batches with varying amounts of this effective, inexpensive, novel additive were prepared with ash from Ash Sample #3. The results are shown in the Table 1. The amount of additive is given as a percentage of the weight of cement present in each batch. A second batch of concrete, Batch Number 44, was made with the last portion of Ash Sample #3, using the same recipe as Batch Number 32.

Samples of ash and concrete were examined in the Scanning Electron Microscope (SEM) in the secondary electron imaging mode. The phases present were also compared using X-ray microanalysis in the SEM. Figures 1 and 2 are examples of micrographs for Batches Number 42 and 44, respectively, in the secondary electron imaging mode. It appears from an examination of these micrographs that, even with a 12-fold increase in additive from Batch Number 42 to Batch Number 44, the same basic cement structure is present in both concretes.

Figures 3 and 4 are SEM micrographs of ash. Figure 3 is for Ash Sample #4 as received. Figure 4 is for Ash Sample #3, which has been mixed with an aqueous solution of the chemical additive, using the same amounts of ash and additive as was used in preparing Batch Number 32. It may be observed from an examination of these micrographs that the surface of the as-received ash is heavily contaminated with fine particles, which are not present on the treated ash.

It is hypothesized from the observations reported above that the elimination of the fine particles in the concrete formulations with the chemical additive renders the surface of the ash particles (serving as fine aggregate) more amenable to strong bonding with the hydrated Portland cement, yielding high-strength concrete as a product.

A preliminary cost analysis of one ton (4400 kg) of concrete (dry basis), composed of

- 420 pounds (930 kg) coarse aggregate
- 750 pounds (1650 kg) of ash
- 830 pounds (1830 kg) of Portland cement
- chemical additive at the level of Batch Number 32

shows that purchase of the materials for its manufacture would require $23.50. The cost of materials for a 2:2:1 precast concrete is $10.00. The ash-containing concrete with the formulation of Batch Number 32 would be $13.50 more expensive than the standard concrete. Since the former contains 750 pounds of ash, the ash would have to be forced into this beneficial use with a tipping fee of $36.00 per ton, which is less than one-third of the current tipping fee at landfills.

FUTURE WORK

One final technical step in developing concrete with the same recipe as Batch Number 32 needs to be taken. Durability tests (tension strength, expansion, freeze/thaw, deicing and abrasion) and a TCLP extraction need to be carried out. When these results are available, precasters in the vicinity of the MSW combustor, operated by the Dutchess County Resource Recovery Agency, can make an informed technical decision on the use of the ash from this combustor in their products.

Regulatory permission for this use of the MSW combustor ash would then have to be sought from the State of New York.

Several other aspects of the beneficial use of MSW combustor ash in Portland cement concrete should be examined. First, the current 0.5:0.9:1 recipe may not be the optimal one for commercial use. A range of formulations should be explored. Second, additives similar to the one used in these first experiments could be tried, especially if durability and TCLP tests uncover any problems. Third, ash from other types of combustors could be tested for the applicability of the new additive . These combustors would include other MSW combustors with different methods for ash removal from the unit. They could also include industrial and hazardous waste combustors.

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TABLE 1. Variation of Compressive Strengths with Additive

Batch Number	Additive (%)	90-Day Compressive Strength, Psi (MPa)
29	3.47	0 (0)*
30	1.73	4940 (34.1)
32	0.87	6200 (42.8)
36	0.65	3750 (25.9)
37	0.43	3210 (22.1)
34	0.17	2260 (15.6)
42	0.07	1560 (10.8)**

* All cylinders of this batch broke apart by 90 days.
** 14-day compressive strength.

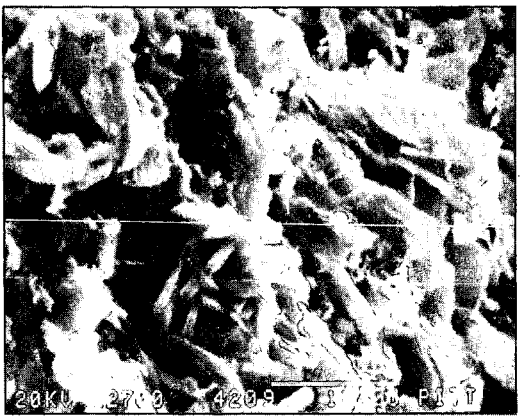

FIGURE 1. SEM micrograph of the fractured surface of Batch Number 42, made with 0.07% additive; the bar is 10 micrometers.

FIGURE 2. SEM micrograph of fracture surface of Batch Number 44, made with 0.87% additive; the bar is 10 micrometers.

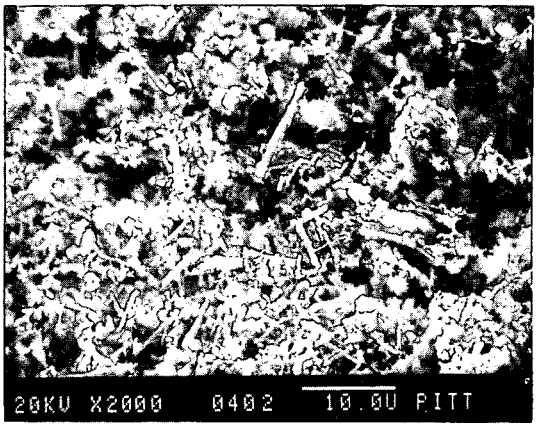

FIGURE 3. SEM micrograph of Ash Sample #4 as received; the bar is 10 micrometers.

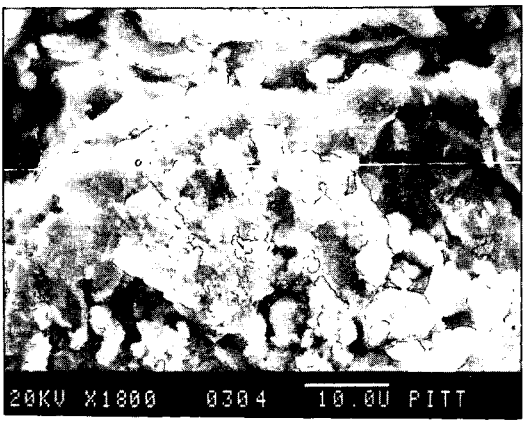

FIGURE 4. SEM micrograph of Ash Sample #3, mixed with additive; the bar is 10 micrometers.

CHARACTERIZATION OF MUNICIPAL WASTE BY SCANNING ELECTRON MICROSCOPY AND OPTICAL MICROSCOPY

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Keywords: municipal waste characterization, waste gasification, microscopy of sewage sludge

ABSTRACT

The use of municipal waste in conjunction with coal gasification is becoming an increasingly attractive option for disposal of this waste. Characterization of the properties of the waste material is necessary before it can be utilized as a feedstock. There are considerable differences in the municipal waste generated by different communities and regions of the country and these differences can affect the gasification process. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Microanalysis (EDX), using a backscattered electron detector, was used to examine the mineral content and morphology of the municipal waste. The fiber content and morphology was also characterized, using both optical microscopy and SEM.

INTRODUCTION

Disposal of municipal waste has been an environmental issue in recent times. Methods of disposing of this waste by incineration and composting have drawbacks. Composting requires space and time, while incineration is wasteful of the energy inherent in the sludge, and distasteful to the public. The continuing development of the coal gasification process allowing incorporation of the sludge as part of the feedstock in this process is an option for the disposal of this waste. Conversion of the sludge to electric power by this process rather than wasting its inherent energy value is the result. In terms of energy conservation this factor makes the process attractive.

There are several processing aspects which must be considered in utilizing municipal waste as a feedstock. Municipal waste must be partially dewatered before it is shipped to the gasification plant. The viscosity of the mixed coal/sludge slurry is important because it must be pumped into the reactor. Beyond the mixing ratio, some of the factors influencing the viscosity of the sludge will be due to the composition of the material, particularly the fiber content.[1] Wastes from different parts of the country and different communities will have different compositions. For instance, municipal waste from Passaic County, NJ is known to have a high content of kaolinite due to the concentration of paper producing plants in the region. Some municipalities produce a sludge with a higher fiber content than others. Minerals containing elements which are volatile at gasification temperatures may be found in

higher concentrations in one region as opposed to another. The nature of the mineral content of the sludge will have an effect on the slag produced and volatile elements may initiate formation of deposits.

Although bulk elemental analysis of sludge is essential to the characterization of the material, microanalysis through the use of optical and scanning electron microscopy techniques and Energy Dispersive X-ray microanalysis also has its place. Municipal waste is an extremely heterogeneous material and examination of this material by these techniques can provide insight on associations of the minerals with the organic content of the sludge and morphology of the fibers. Presented here are the results of microscopic characterizations performed on raw and treated samples of dewatered sludge from Los Angeles County, CA, and Passaic County, NJ.[2]

EXPERIMENTAL

SAMPLE PREPARATION

For the SEM analysis, a small amount of each sample was mounted and carbon coated using an evaporative coater to produce a conductive surface. In addition, several of the LA County samples were sputter coated with gold in order to obtain improved imaging results for documentation. The optical microscopy was performed on larger portions of the sludge.

OPTICAL MICROSCOPE

A Nikon SMZ-10 stereoscopic optical microscope was used to take color photomicrographs of the raw and treated LA County, CA municipal waste.

SCANNING ELECTRON MICROSCOPE

The instrumentation used for this study was an AMRAY 1645 SEM equipped with a lanthanum hexaboride (LaB6) electron emitter source and imaging detectors for secondary and backscattered electrons. A Tracor Northern TN-5500 Energy Dispersive X-ray microanalysis system (LSI 11/73 CPU with 3 MByte working memory and 30 MByte mass storage capacity) with a lithium-drifted silicon detector was used for semiquantitative analysis of elements with an atomic number greater than 10 and less than 92. Elemental spectral analysis was performed using standardless software routines with ZAF correction factors. The SEM conditions for analysis were 20KV acceleration voltage, 100 micron emission, 200 micron final aperture, spot size 4, working distance 24 millimeters, 0 degrees tilt, and a calculated take-off angle of 28.6 degrees. In addition to elemental analysis and photomicrography, X-ray mapping and digital image acquisition were performed on the LA County samples.

RESULTS

Optical microscopy was used to get an overview of the morphological characteristics of the municipal waste. As the figures show, the raw sludge contained a large amount of fibrous material. In addition, sprouting seeds and plastic bandage materials were found. The treated sludge materials looked darker and more granular, with little fibrous material present.

SEM/EDX microanalysis was used to verify these results and to characterize the mineral content of the waste material. It is important to understand that only a small portion of sludge was examined by microanalysis and therefore the elemental analysis is not representative of the bulk of the municipal waste.

Morphological study by both methods indicated that many of the untreated sludge particles were held together by fibrous material, mostly hair and cellulosic plant fibers. In the LA County sludge, the hair was usually long and curled around the organic material while the plant fibers which were present were thicker and often served as a base on which the organic material could anchor. The Passaic sludge was matted together, with short fibers holding the organic material together in a matrix.

Seen in the untreated LA County sludge, along with the discrete woody cellulosic materials, fibers, and mineral particles, were many particles of organic material. These had inclusions of smaller particulate mineral matter, which were often silicates. Also included within the organic matrix were fibers, woody material and even plastics or spongy material. Other inorganic mineral matter found within the matrix of these samples contained iron, barium, aluminum, zinc, magnesium, phosphorus, calcium, sulfur, potassium, and titanium. In addition to these elements, a Houston municipal waste which was characterized contained cadmium, nickel, and lead. The treated LA sludge samples were devoid of the fibrous and cellulosic material. Mineral inclusions were still present within the matrix of the organic material.

The backscattered electron detector was used to locate particles containing inorganic elements and to obtain photomicrographs when charging problems prevented good imaging by secondary electrons. X-ray mapping was useful in locating associations between elements on a broader scale. Figures 1 and 2 show the labeling of the analyzed points of solid sludge particles. The tables beneath these figures give the EDX microanalysis of the marked points. The other figures present morphological information about the different municipal wastes.

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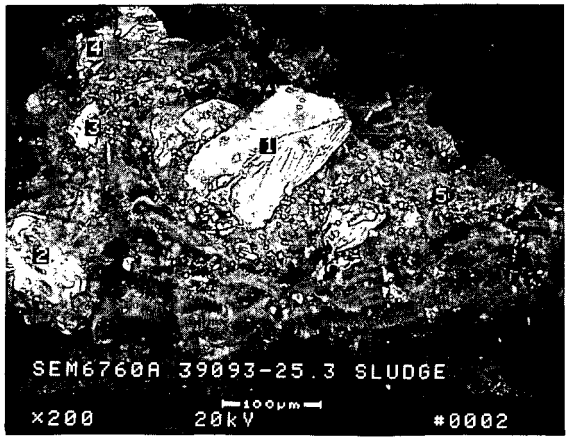

Fig.1 Los Angeles Raw Sludge (200X): A particle of sludge composed of both mineral matter and organic matter.

Analysis Table (normalized results):

ELEMENTAL ANALYSIS (WEIGHT % OF MINERAL MATTER)

POINT	Mg-K	Al-K	Si-K	P-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Fe-K	Cu-K	Ni-K	Zn-K
1	--	1	94	1	1	--	-	--	--	--	3	--	--
2	1	6	3	1	1	--	7	2	3	64	9	1	2
3	1	4	1	-	1	--	-	14	1	73	5	--	-
4	5	17	2	-	1	3	-	--	-	24	41	2	4
5	2	10	19	15	13	3	1	18	2	10	5	1	1

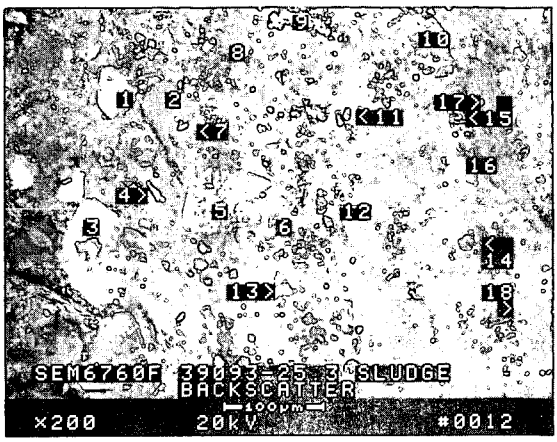

Fig.2 LA County Raw Sludge (200X): Portion of a sludge particle showing its heterogeneous nature.

Analysis Table (normalized results):

ELEMENTAL ANALYSIS (WEIGHT % OF MINERAL MATTER)

POINT	Mg-K	Al-K	Si-K	P-K	S-K	Cl-K	K-K	Ca-K	Ba-K	Ti-K	Fe-K	Cu-K	Zn-K
1	--	--	96	1	-	--	-	--	--	--	1	1	--
2	--	2	2	2	78	2	-	3	--	--	4	5	1
3	--	1	92	1	-	--	-	--	--	--	1	4	--
4	--	5	3	1	2	1	1	24	--	1	51	9	2
5	--	1	96	-	-	--	-	--	--	--	--	2	--
6	2	8	14	17	12	1	1	16	--	2	23	3	1
7	1	2	4	5	24	1	-	3	50	1	8	2	-
8	3	8	10	9	24	3	1	16	--	-	14	10	1
9	2	5	2	1	1	-	-	1	--	4	84	1	-
10	1	1	1	1	-	-	-	95	--	--	1	1	-
11	--	25	56	1	1	1	-	14	--	--	1	1	-
12	2	10	15	6	19	4	3	18	--	--	11	10	1
13	--	1	92	2	1	-	-	--	--	--	1	2	-
14	12	19	30	-	1	-	-	1	--	--	35	1	-
15	--	4	17	7	11	1	6	23	--	3	14	9	5
16	--	--	96	1	-	-	-	--	--	--	1	1	-
17	20	6	47	4	7	1	1	4	--	--	6	3	1
18	2	4	5	9	12	29	1	18	--	6	11	3	-

Fig.3 Los Angeles County Raw Sludge (6X) Optical Photomicrograph: The fibrous material holding this piece together is visible, along with some particles of inorganic material.

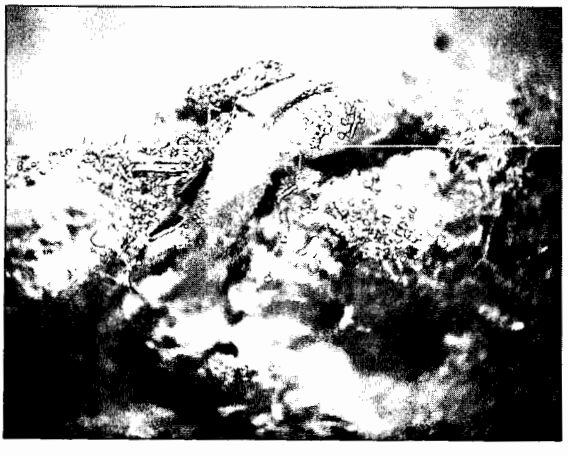

Fig.4 Los Angeles County Raw Sludge (18X) Optical Photomicrograph: A sprouting seed found in this municipal waste.

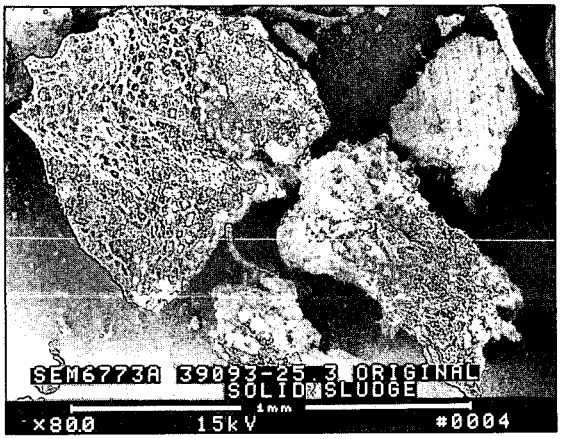

Fig.5
Raw LA County Sludge (80X): The honeycombed particle was aluminum silicate, the upper right corrugated particle was cellulosic, and two lower ones were organic matter with mineral inclusions.

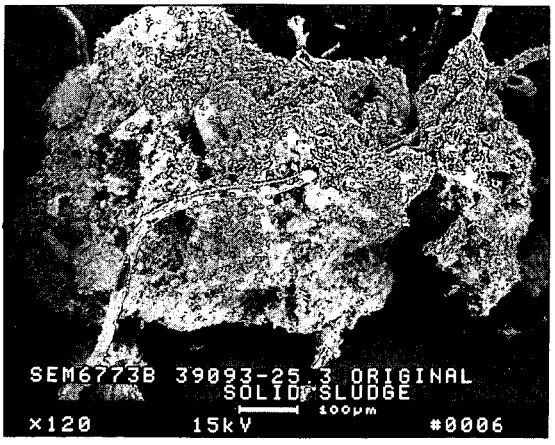

Fig.6 Raw LA County Sludge (120X): Organic particle with fibers and mineral particles included in the matrix.

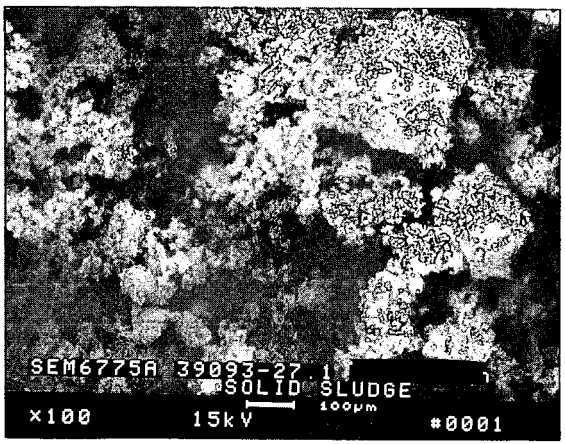

Fig.7 LA County Sludge after treatment process (100X): Fibers have disappeared and material is more homogeneous.

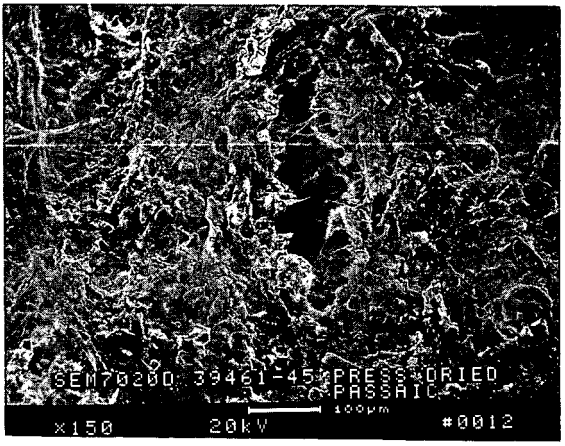

Fig. 8 Passaic Valley, NJ Sludge (150X): Fibrous sludge with mat-like morphology.

Trace Metals Analysis of Fly Ash by Inductively Coupled Plasma Atomic Emission Spectrometry

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A binding agent has been developed for pelletized densified refuse derived fuel (dRDF). Initial studies showed that calcium hydroxide ($Ca(OH)_2$) is effective in reducing the rate of biological and chemical degradation of dRDF pellets. A commercial test of dRDF, with $Ca(OH)_2$ as a binder, was conducted at Jacksonville, Florida Naval Air Station in the summer of 1985.

In June/July of 1987 a full-scale cofiring of a binder densified refuse derived fuel (bd-RDF) and high sulfur content coal was conducted at Argonne National Laboratories (ANL). About 567 tons of bd-RDF pellets was cofired with coal, at 0, 10, 20, 30, 50 percent d-RDF Btu content and 0, 4, 8 percent calcium hydroxide binder. Results indicated that some trace elements decreased in fly ash with the increase in dRDF percentage while others increased.

The most toxic elements of concern are As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V and Zn. A microwave oven dissolution method was used to dissolve the ash in a mixture of aqua-regia and hydrofluoric acid using a Parr bomb. The solution was then analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy after approximate dilution.

Introduction

Incineration of municipal solid waste is an attractive solution to landfills[1-4] . However the physical and chemical characteristics of ash are becoming more and more important for safe disposal[5] . Some trace metals are important in the ash because of their potential toxicity, which plays a role in characterizing the ash as hazardous, and how and where to dispose of it.

Mass burn incineration produces ash residues amounting to 15 to 25 percent by weight and 5 to 10 percent by volume of the incoming Municipal Solid Waste (MSW)[3,6] . Ash comes in two forms. Fly ash the fine particles in the flue gas collected by electrostatic precipitators or bag house, and bottom ash the material dropped from the grate in the furnace. The ashes during the 1987 study at ANL were collected three times a day for six weeks from both the bag house and the grate.

Trace element concentrations in ash are of great interest because of their relationship to regulatory criteria under the Resource Conservation and Recovery Act (RCRA) regarding toxicity. Trace metals in fly ash were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Several investigators have examined the feasibility of ICP-AES for the rapid, precise, and accurate multi-element analysis[7-13]. ICP-AES permits the determination of a large number of elements with high sensitivity and precision and with relative freedom from chemical interferences[14-17].

Methodology

Fuel Preparation

The binder enhanced d-RDF pellets for the 1987 ANL study were supplied by two facilities, one located at Thief River Falls, (Future Fuel Inc.) Minnesota, and the other at Eden Prairie, Minnesota (Reuter Inc.). The dRDF was made with 0, 4, 8 percent $Ca(OH)_2$ binder. High-sulfur Kentucky coal is normally burned in the power plant of Argonne National Laboratory at the rate of nine tons per hour.

Before each test run, d-RDF pellets and coal were blended together using a front-end loader until the material looked roughly homogenous. Three volumes of coal and one volume of d-RDF produces a blend close to 10 percent d-RDF by Btu content. Then the blend was moved by front-end loader to the coal pit and transported by conveyor to coal bunker prior to use in the ANL stoker fired boiler.

Sampling Plan

A total of 567 tons of d-RDF pellets were cofired with 2,041 tons of sulfur-rich coal in 12 test runs. The runs were classified according to the different Btu contents of d-RDF in the fuel and different binder content of d-RDF. Runs 1 and 12 used coal alone in order to establish base line data. In between the different runs and to avoid cross-contamination, coal runs were performed to cleanout the d-RDF from the previous run. Details of the test plan and sampling locations have already been published[3,18,19,20].

Sample Collection

During the test runs, samples were collected from various plant locations that were of interest in the study. Economizer, multicyclone fly ash and bottom ash samples were collected in aluminum containers and then transferred to plastic zip-lock bags for subsequent analysis at the University of North Texas.

Equipment

Parr Bombs

Parr Teflon acid bombs were obtained from Parr Instrument Company. The bomb is made of a microwave transparent polymer. A compressible relief disc is built into the closure to release excessive pressure. Over 1500 psi the relief disc will be compressed to a point where support for the O-ring will be lost and it will blow out. In most cases all parts of the bomb were reusable except for the O-ring.

Microwave Oven.

A Kenmore commercial microwave oven was used in this work. The oven has a variable timing cycle from 1 second to 100 minutes and a variable heating cycle based on power setting from 10% through 100% full power (700 w).

Inductively Coupled Plasma Atomic Emission Spectrometry ICP-AES

A Perkin-Elmer ICP-5500 Atomic Emission Spectrometer with a 27.12-MH$_z$ RF generator was used in this analysis. A Perkin-Elmer Model-10 data station was used with a Pr-100 printer.

Sample Analysis

After the samples were returned to the laboratory, they were arranged on the shelves according to the dates and times they were collected. About 10 grams of a homogenous sample was ground to pass at least a 75 mesh sieve. A 400 mg sample was placed in a polyteflon container and treated with 1 mL of hydrofluoric acid and 3 mL of aqua regia. The teflon container was then placed in the bomb and the bomb was tightly capped. The bomb was placed in the microwave oven and heated for 4 minutes and left for several hours to cool. After cooling, the PTFE container was uncapped and 2 mL of saturated boric acid was added quickly. The container was then recapped, returned to the microwave oven and reheated for 1 more minute, then cooled again.

At this stage some uncombusted carbon remained, so the solution with the residue was filtered, washed with deionized water and the filtrate was diluted to 50 mL in a polyethylene volumetric flask.

The microwave heating procedure has been used to determine minor and major constituent in the past. The solution was finally analyzed by ICP-AES using a blank and a standard solution containing the same amounts of acids. Standards with varied concentrations of As, Hg, Pb, Sb, Se, Tl, Ba, Be, Cd, Cr, Cu, Ni, V, Zn, were used for the analysis.

Results and Discussion

The chemical composition of coal/dRDF ash depends on geological and geographic factors related to the coal deposits, the combustion conditions and the efficiency of air pollution control devices. The fly ash samples which were investigated by ICP-AES were the Economizer fly ash samples. The results are summarized in Table 2. Thirteen elements were investigated; As, Cd, Hg, Pb, Sb, Se, Te, Ba, Be, Cr, Cu, Ni, V, and Zn. The metals As, Cd, Hg, Pb, Sb, Se and Tl are not included in the table because their concentrations were too low to be detected by ICP. Table 3 shows the ICP detection limits of all elements studied.

Effect of d-RDF content on trace metals:

Processing of MSW to RDF removes much of the unwanted trace metals. The metal content of coal/RDF blend ash is expected to be affected by the different percentages of RDF.

The trace metal concentration is economizer fly ash are listed in Table 2. Elements such as Cd, Cr, Cu, Hg, Pb and Zn are known to be enriched in RDF related to coal.

Table 2 and the graphs shows the percent bd-RDF versus concentration (ug/g) for each element alone at a constant level of binder. The top graph shows 0, 10, 20 ,30 percent bd-RDF versus element concentration at 0 percent binder. The middle graph shows the 10,20,30,50 percent bd-RDF versus element concentration at 4 percent binder. The bottom graph shows the concentrations at 8 percent binder. The graphs shows how the elements are increasing or decreasing in concentration with the increase in bd-RDF.

From Table 2 and the graphs, the most prominent increase in concentration resulting from cofiring coal/RDF mixtures were Cu and Zn. Ba and Cr were increased slightly in economizer fly ash. This increase is due to these elements being more enriched in RDF ash than in coal ash, while Be, Ni and V content were lower or close to those in coal ash.

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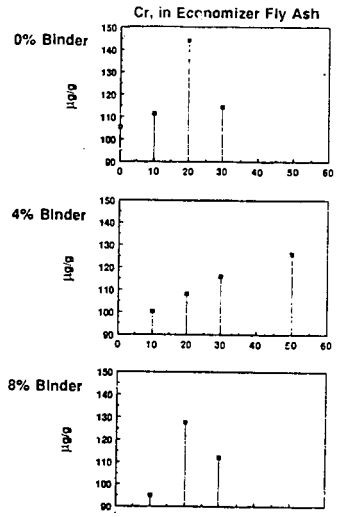
Table 2. Summary of Toxic Metals Concentration in Economizer Fly Ash (ug/g).*

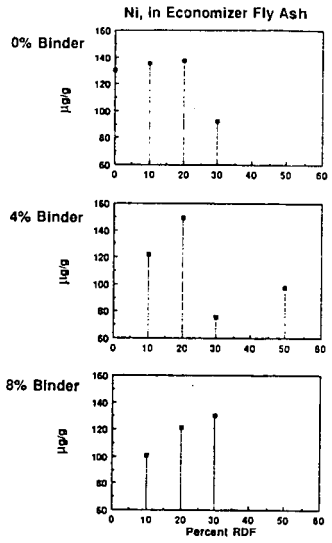
Run#	Ba	Be	Cr	Cu	Ni	V	Zn	Btu%dRDF	Binder%
1.	158.2	25.3	105.2	152.7	130.0	223.4	324.8	0	-
2.	240.1	27.7	111.3	199.5	135.3	234.1	338.5	10	0
3.	202.2	19.6	100.3	151.8	122.2	177.9	293.7	10	4
4.	144.4	14.7	94.9	143.7	100.8	160.7	390.8	10	8
5.	227.7	20.2	143.8	243.4	137.4	231.0	404.6	20	0
7.	155.7	11.3	108.3	208.5	149.0	187.1	478.2	20	4
8.	182.8	13.3	127.6	243.6	121.3	193.4	466.7	20	8
9.	160.1	11.4	114.4	360.6	92.7	181.3	443.6	30	0
10.	158.3	10.5	115.9	207.9	75.6	149.6	455.9	30	4
6.	190.2	10.5	112.2	227.6	130.5	161.3	470.8	30	8
11.	228.5	14.9	126.1	353.5	97.7	179.8	372.1	50	4
12.	177.4	16.6	93.5	217.1	97.8	171.6	240.3	0	-

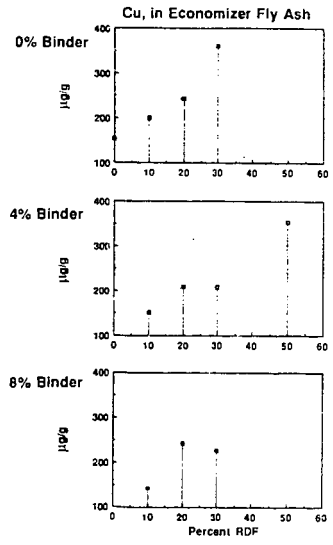
* Average of Three Replicates.

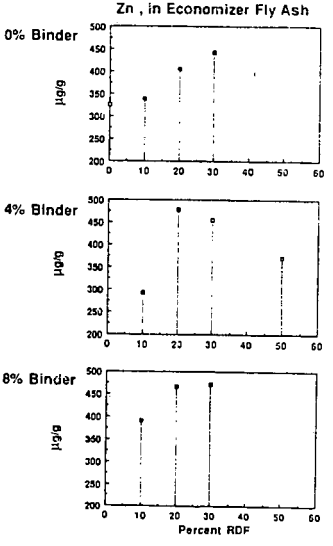
Table 3. Detection Limits of ICP (ug/g).

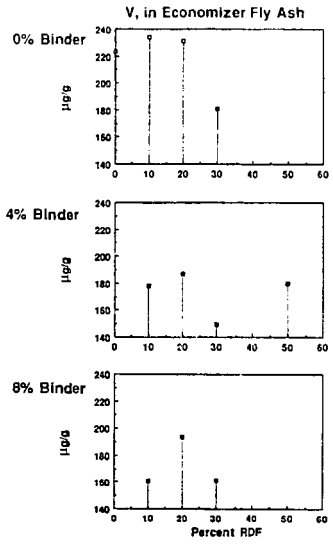
As (ug/g)	62.5
Ba	12.5
Be	0.63
Cd	6.25
Cr	6.25
Cu	6.25
Hg	125.0
Ni	12.5
Pb	125.0
Sb	125.0
Se	62.5
Tl	125.0
Zn	6.25

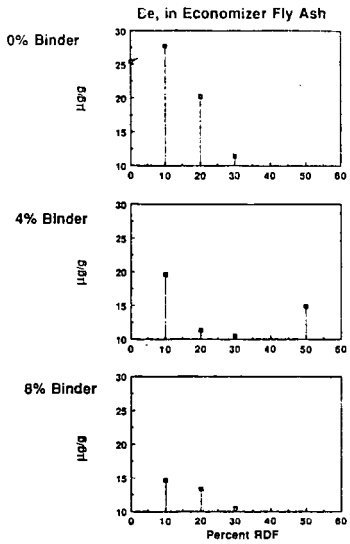

Cr, in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g

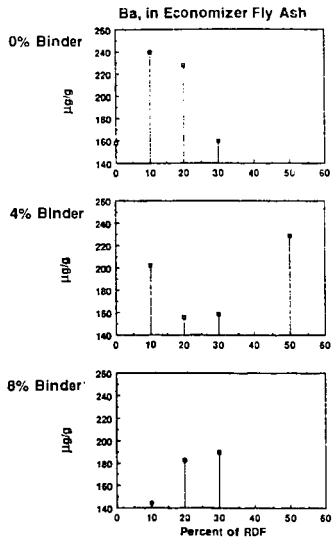

Ni, in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g
Percent RDF


Cu, in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g
Percent RDF


Zn , in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g
Percent RDF


V, in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g
Percent RDF


Ce, in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g
Percent RDF


Ba, in Economizer Fly Ash
0% Binder
4% Binder
8% Binder
µg/g
Percent of RDF

PHASE CHARACTERIZATION OF UNMODIFIED PETROLEUM COKE AND COAL GASIFICATION SLAGS

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Keywords: coal-ash, petroleum-coke, slag, phase characterization

ABSTRACT

The slags produced in gasifiers using petroleum coke as a feedstock differ compositionally and texturally from the ash and slag formed during combustion of coal. Hence, the chemical and slagging behavior of petroleum-coke ash under gasification conditions must differ markedly from the behavior of coal ash. Whereas the latter is reasonably well understood, the former has been much less well studied. The present work is part of an ongoing study aimed at understanding the physical and chemical characteristics of the phases formed in the slags that are produced during petroleum coke gasification.

INTRODUCTION

The partial oxidation of liquid hydrocarbonaceous fuels such as petroleum products and slurries of solid carbonaceous fuels such as coal and petroleum coke to form alternative fuels is now a common practice. An evolving trend in the feedstocks for such processes is that they are becoming increasingly heavy and of poorer quality. To compensate for this trend, refiners must employ more "bottom of the barrel" upgrading to provide the desired light products. The current industry workhorse to provide this upgrading is some type of coking operation (either delayed or fluid). A good deal of current refinery expansion includes the installation or expansion of coker units, and this coking will be a process of general use for some time to come.

The production of light hydrocarbon fuels from coal or petroleum feedstocks results in the formation of ash or slag which concentrates most of the contaminants originally present in the coal or petroleum. Coals contain significant amounts of clays, quartz, pyrite, and carbonates, along with a broad range of less abundant solid mineral phases (Jenkins and Walker 1978). Petroleums contain less solid mineral matter but may contain significant amounts of other contaminants such as iron, nickel, vanadium and sulfur. Consequently, the residual concentration of elements is significantly different depending upon the feedstock materials. The resulting phases affect gasifier operation and the ultimate use or disposal of the ash or slag.

PROCESS DESCRIPTION

The Texaco Gasification Process is a partial oxidation reaction to produce mixtures of CO and H_2, known as synthesis gas. A carbon containing feedstock is reacted with a controlled, sub-stoichiometric quantity of oxygen in a fuel rich, exothermic reaction. The process is carried out in a pressurized reaction chamber with the temperature maintained above the melting point of the coal or petroleum-coke ash, thus making a slag (molten ash), by controlling the individual feed rates of the reactants. The feeds are introduced together, through the top of the gasifier, and pass through it concurrently with the product gases transporting the solids, making it an entrained flow gasifier. It is fundamentally a simple system that leads to high reliability, and it can be adapted readily to fit many applications economically.

The chemical reaction path is quite complicated, and includes many simultaneous and sequential reactions such as devolatilization, combustion and interactions between the feeds and intermediate or final products. The chemistry is depicted in a schematic sense in Figure 1. The conversion of feedstock slurry to synthesis gas is normally in excess of 95% and can be over 99%.

The use of coal as a feedstock, either in direct combustion or as a gasifier feedstock results in most of the ash being converted to slag, a nearly carbon-free, inorganic material. After water quenching, the slag is normally a glass-like solid, with a maximum size of one-half inch. In all cases evaluated to date, the slag from coal gasification, including the fine fractions that are co-mingled with carbon-rich char, have been classed as a non-hazardous waste.

The high temperature gases, char and molten ash, or slag, produced in the gasifier are normally cooled prior to cleanup, by either of two methods: quenching, i.e., direct contact with water, or indirect heat exchange to make high pressure steam in a special syngas cooler.

The molten slag is cooled with the gas and is collected in a water pool either in the bottom of the radiant cooler or in the quench vessel located under the gasifier. The slag is removed from the system by means of a water-filled lockhopper system. The carbon-rich char can be disposed of with the slag or separated for recycle.

The cooled gas is scrubbed with water to remove the remaining fine particulates. Following particulate scrubbing, gas purification is completed by sulfur removal. A variety of subsequent processes can then be used, with the choice made to fit the overall project needs. The cleaned gas can be used for many purposes, such as fuel for power generation or process heat, synthesis of ammonia or other chemicals, or as a reducing gas.

SAMPLE PREPARATION AND ANALYSIS

The slag samples examined in this study occur both as fragmental materials that are discharged routinely from the gasifiers and as solid incrustations that build up on the interior walls of the gasifier. Megascopically, most samples appear as dark brown to black, porous to solid, irregular masses ranging from less than one-fourth to more than several inches across. The samples removed from the gasifier walls are commonly layered, apparently reflecting episodic buildup.

Representative portions of slags were cast in a low viscosity, cold-setting epoxy resin. Porous samples were vacuum impregnated by placing them in a vacuum desiccator in which vacuum was alternated with normal air pressure. This procedure removed trapped air and forced the epoxy into pores and cracks. Samples were then polished using standard techniques employed for optical microscopy and electron microprobe analysis as described in Craig and Vaughn (1981).

GASIFIER SLAGS

Characterization of slags produced in gasifiers is important in determining the ultimate use and/or disposal of the slags. Furthermore, a prior knowledge of the nature of the slag phases is necessary if it becomes desirable to alter slag properties that adversely affect the operability of gasifiers. To these ends, we have been carrying out investigations on the physical and chemical properties of slags produced both from coal and from petroleum coke feedstock. The slags produced from the different feeds are markedly different, as evidenced in the data presented in Table 1, 2, and 3.

The conditions under which coal and petroleum-coke ash and slags form are similar in that they all involve partial to full combustion. The principal difference is that direct combustion is generally more oxidizing and hence will permit formation of more oxidized phases (eg. ferric rather than ferrous phases). Coal bottom ash, fly ash, and slags have been examined by numerous investigators in recent years as noted in Table 2 and by a wide variety of techniques (eg. Huggins and Huffman, 1979; Weaver 1978; Voina and Todor, 1978; Eriksson et al. 1991). Typical coal ash as noted in Table 1 is rich in SiO_2 with major but variable amounts of Al_2O_3, Fe_2O_3, and CaO. Coal slag are generally dominated by glass phases which, though highly variable, are always rich in SiO_2 and contain significant Al_2O_3. Some glasses are also sufficiently rich in reduced iron to be referred to as "ferrous glasses" (Huffman et al. 1981). The number and variety of other mineral analogous

phases are considerable (Table 2) but often constitute only small proportions of the bulk material. Furthermore, several percent unreacted or partially reacted carbon-char are commonly present.

The glass phases display flow, banding, indicating some flow of compositionally distinct zones. Crystalline phases range from skeletal to fibrous laths (commonly mullite or anorthite; Hulett et al. 1980; Huggins et al. 1981) to skeletal and cruciform spinels (Chen et al. 1986).

Petroleum-coke slags are also highly variable in composition but generally contain less SiO_2, less Al_2O_3 and less CaO but greater amounts of Fe_2O_3, V_2O_5, NiO and sulfur (included in "others" Table 1). The iron and vanadium contents are reported as given by ASTM analytical procedures; however, iron and vanadium actually occur in lower oxidation states in these slags. These gross compositional differences reflect the nature of the source materials. Coals contain abundant included clays and carbonate minerals, whereas petroleum contains less discrete fragmental mineral matter but often contains significant amounts of organic sulfur and porphyrins that hold iron, nickel, vanadium, and chromium.

A general result of these differences in composition is the fusibility of the ash. Typical coal ash has initial deformation (ID) temperatures of 2120°-2140° F, softening temperatures (ST) of 2150°-2210°F, and fluid temperatures (FT) of 2250°-2430° F. In contrast, typical petroleum coke ash remains undeformed and does not melt until temperatures exceed 2700° F.

PETROLEUM COKE SLAGS

The present study has concentrated especially on slags formed during gasifier operation using petroleum coke without any additives to alter constituents or behavior, and are part of an ongoing study to characterize the physical and chemical characteristics of such slags (Craig et al. 1990; Craig and Najjar 1990; Groen et al. 1991).

The investigators have found that the slags formed, display a variety of textures and phases; these apparently reflect differing locations and hence conditions within the gasifiers as well as differences in the feedstock. In general, the types of slags may be summarized as (1) glass-rich, (2) V-oxide rich, (3) sulfide-rich, (4) CaMgFe-silicate-rich. These no doubt represent end members of a continuum, but most samples extracted from the gasifiers conveniently fall into one of these categories. The total of the wide variety of phases that the investigators have found to date are listed in Table 3. Below briefly described are each of the major types of slags noted above:

Glassy Slags - These generally range from black to brown glasses that occasionally exhibit well developed flow textures evidencing their slow flow down the sides of the gasifier. Typically, they contain significant quantities of very fine spherical iron sulfide droplets. The droplets greater than 1 mm in diameter appear to have been formed along with the glass. Finer droplets, down to less than 1 micrometer, appear to have formed primarily through exsolution on cooling. Glassy slags commonly contain dispersed skeletal to cruciform spinels which also appear to have formed on cooling as the liquidus boundary was intersected.

V-oxide-rich slags - These slags are relatively SiO_2-poor and represent slag formation within the gasifier where vanadium phases crystallize as relatively coarse crystals (~100 micrometers). The V-oxide phases occur as interlocking laths with interstitial spinel crystals and droplets of glass and sulfide-oxide intergrowths. The coarseness of the crystals and the absence of flow structures and exsolution features indicate that the V-oxide phases were stable and forming directly under the conditions of gasifier operation.

Sulfide-rich Slags - Many chunks of slag consist primarily of intimate iron sulfide-iron oxide intergrowths. The iron sulfide ranges from pure FeS (troilite) to $Fe_{1-x}S$ (hexagonal pyrrhotite) and the iron oxide is FeO (wustite). The intergrowths are symplectic in nature and are often so fine (1 micrometer and less) that they are barely resolvable with an optical microscope. The textures are characteristic of the unmixing of phases from a homogenous melt on rapid cooling. Nickel may substitute on a minor scale for the iron in the pyrrhotite and may, in nickel-rich areas, occur as Ni_3S_2 (heazlewoodite) or as $(Fe, Ni)_9S_8$ (pentlandite). The iron sulfide-iron oxide masses commonly contain dispersed drop-like to cruciform crystals of free iron-nickel alloy. Also scattered throughout

the sulfide-oxide matrix are droplets of glass and euhedral to skeletal iron aluminum spinels which may concentrate significant amounts of vanadium and chromium.
CaMgFe-silicate slags - These occur as local segregations within sulfide-rich slags. The sulfide phase cannot accomodate Ca, Mg, or Si within its structure, hence these elements concentrate sufficiently to form a variety of CaMgFe silicates.

SUMMARY

It is apparent that the differences in the bulk chemistries of the petroleum coke and coal slags are reflected in the behavior and nature of the phases within each. The high silica and alumina contents of the coal slags result in lower melting temperatures and the development of predominantly glassy products. In contrast, the low silica and alumina contents of the petroleum coke slags, coupled with high transition metal contents, result in the development of a variety of crystalline phases. Most notable are aluminate spinel phases that concentrate iron, vanadium, chromium and nickel, and sulfide-oxide intergrowths in which nickel becomes concentrated in both sulfide and accessory alloy phases.

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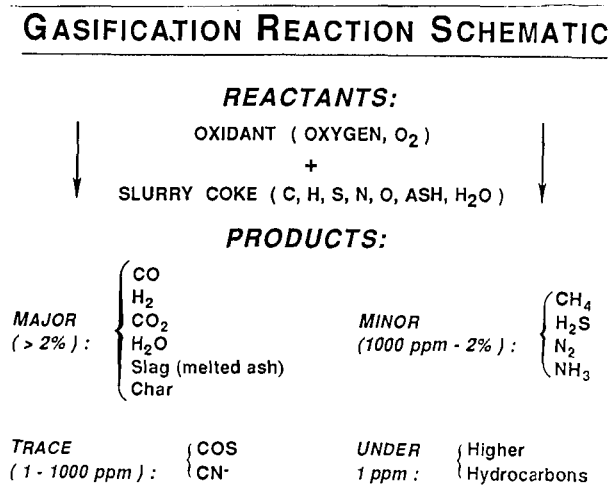

Figure 1. Simplified schematic diagram of the partial oxidation reaction occurring in a petroleum coke gasification.

Table 1. Typical ash composition in wt % of coal and petroleum-coke generated ash.

	Coal		Petroleum Coke	
	Eastern	Western	Type A	Type B
SiO_2	52.1	42.0	4.4	40.6
Al_2O_3	15.4	25.0	1.5	9.6
Fe_2O_3	7.3	20.9	23.0	6.3
CaO	17.4	9.5	7.5	1.4
MgO	3.7	--	--	2.4
NiO	--	--	20.9	14.0
V_2O_5	--	--	40.3	16.6
Others	4.1	2.6	2.5	9.1
Carbon %	9.5	9.7	0.5	0.9
	Ash Fusibility, °F			
ID	2120	2140	--	--
ST	2150	2210	--	--
FT	2250	2430	>2700	>2700

TABLE 2.

COAL COMBUSTION ASH / SLAG PHASES

Phase Composition	Remarks	Mineral Name	Reference
FREE ELEMENTS:			
C	unreacted char	Graphite	Quon et al., 1984
FeSi	- - - - - - -	- - - - - - -	Quon et al., 1984
SULFIDES:			
FeS	- - - - - - -	Troilite	Huffman et al., 1981
$Fe_{1-x}S$	- - - - - - -	Pyrrhotite	Huffman et al., 1981
SULFATES:			
$CaSO_4$	Result of Ca from calcite reacting with SO_2	Anhydrite	Huffman et al., 1981
OXIDES:			
FeO	- - - - - - -	Wüstite	Huffman et al., 1981
Fe_3O_4	- - - - - - -	Magnetite	Quon et al., 1984
$(Fe,Al)_3O_4$	- - - - - - -	Hercynite	Huffman et al., 1981
Ferrite phases	Cited as mostly Fe_3O_4	- - - - - - -	Huffman et al., 1981
Ferrite phases	Cited as calcium ferrite	- - - - - - -	Huggins et al., 1981
$Fe_{3-x}M_xO_4$	M = V, Cr, Mn, Co, Ni, Zn	Spinels	Hulett et al., 1980
Fe_2O_3	In oxidized ash	Hematite	Quon et al., 1984
Al_2O_3	- - - - - - -	Corundum	Huggins et al., 1981
TiO_2	- - - - - - -	Rutile	Quon et al., 1984; Chen et al., 1986
SiO_2	- - - - - - -	Cristobalite	Quon et al., 1984; Chen et al., 1986
SiO_2	Residual phase ?	Quartz	Hulett et al., 1980; Hulett and Weinberger, 1980; Raask, 1982; Quon et al., 1984; Chen et al., 1986
Glass	Highly variable Si-Al-dominated ferrous glass	Obsidian	Fessler et al., 1980; Huffman et al., 1981; Raask, 1982; Quon et al., 1984; Chen et al., 1986
Silicates:			
Fe_2SiO_4	- - - - - - -	Fayalite	Huffman et al., 1981
$Al_6Si_2O_5$	- - - - - - -	Mullite	Hulett et al., 1980; Hulett and Weinberger, 1980; Raask, 1982; Quon et al., 1984; Chen et al., 1986
$CaAl_2Si_2O_8$	- - - - - - -	Anorthite	Huggins et al., 1981; Quon et al., 1984
$Ca_2Al_2SiO_7$	- - - - - - -	Gehlenite	Huggins et al., 1981

TABLE 3.

PETROLEUM COKE GASIFIER SLAG PHASES

Phase Composition	Texture	Ideal Composition	Mineral Name
FREE ELEMENTS:			
FeNi-alloys (up to >70 atomic percent Ni)	Dendritic to blocky crystals & irregular blebs all in sulfide matrix	Complete Fe to Ni solid solution	Native Iron & Native Nickel
C	Aggregates of radiating to fibrous microcrystalline subgrains	C	Graphite
SULFIDES:			
(Fe,Ni)S	Matrix phase often symplectic with "FeO", & as irreg. blebs in glass	FeS	Troilite
$(Fe,Ni)_{1-x}S$	Matrix phase often symplectic with "FeO", & as irreg. blebs in glass	$Fe_{1-x}S$	Pyrrhotite
$(Fe,Ni)_9S_8$	Irregular separations in sulfide matrix	$(Fe,Ni)_9S_8$	Pentlandite
$(Ni,Fe)_3S_2$	Irregular blebs in V-oxide rich slags	Ni_3S_2	Heazlewoodite
CeS	Irregular blebs	(Ce,Mn)S	Oldhamite
$(Fe,Ni,Cr)VS_3$	Dendritic crystals in sulfide matrix	-------	-------
Undeciphered sulfides	Euhedral micron-scale crystals in sulfide matrix	-------	-------
SULFATES (?) :			
Undeciphered Ni-S-O phases	Euhedral micron-scale crystals in sulfide matrix	-------	-------
OXIDES:			
(Fe,Mg,V,Ni)O	Symplectically intergrown in sulfide matrix, and as dendritic crystals and rounded blebs in sulfide matrix	FeO	Wüstite
(Ni,V,Fe)O	Alteration rind on bleb of $(Ni,Fe)_3S_2$	NiO	Bunsenite
$(Fe,Ni,Mg)(Fe,Al,V)_2O_4$	Euhedral massive crystals in V-oxide rich matrix	Fe_3O_4	Magnetite

Phase Composition	Texture	Ideal Composition	Mineral Name
$(Fe,Mg)(Cr,V)_2O_4$	Euhedral crystals in glassy matrix (residual from refractory brick?)	$FeCr_2O_4$	Chromite
$(Mg,Fe)(Cr,Fe,Al,V)_2O_4$	Euhedral crystals in glassy matrix (residual from refractory brick?)	$MgCr_2O_4$	*Magnesiochromite*
$(V,Cr)V_2O_4$	Euhedral massive crystals in sulfide matrix	V_3O_4	-------
$(Fe,V,Cr,Ni)V_2O_4$	Euhedral massive to dendritic crystals in sulfide matrix	FeV_2O_4	Coulsonite
$(Mg,Ni,Fe)(Al,V,Cr,Fe)_2O_4$	Euhedral massive to dendritic crystals in V-oxide rich matrix	$MgAl_2O_4$	Spinel
$Fe(Al,Fe)_2O_4$	Irregular grains w/ FeS interstitial between dendritic FeO crystals	$FeAl_2O_4$	Hercynite
$(Ni,Fe)(Fe,Al)_2O_4$	Euhedral skeletal crystal in V-oxide rich matrix	$NiFe_2O_4$	Trevorite
$(Ni,Mg)(V,Fe,Al,Cr)_2O_4$	Euhedral massive crystals in V-oxide rich matrix	-------	-------
$(Fe,V,Al,Cr)_2O_3$	Oxidation crusts on sulfide-rich and glassy slag surfaces	Fe_2O_3	Hematite
$(Cr,Fe,Al,V)_2O_3$	Exsolved lamellae in chromite crystals	Cr_2O_3	Eskolaite
$(Al,Fe,V,Cr)_2O_3$	Slender acicular crystals & as irregular cores of spinel crystals	Al_2O_3	*Corundum*
$(V,Fe,Cr)O_2$	Bladed euhedral crystals in V-oxide rich slag	VO_2	-------
$(V,Al,Fe,Cr)_2O_3$	Crusts on Fe-Ni sulfide/oxide symplectic intergrowths	V_2O_3	Karelianite
$(Ca,Mg,Ni)V_2O_6$	Bladed to feathery euhedral crystals in V-oxide rich slag	CaV_2O_6	-------
$(Fe,Mg,Ni)(V,Al,Fe)_2O_5$	Prismatic diamond-shaped euhedral crystals in V-oxide rich slag	FeV_2O_6	-------
$(Na,Fe)(V,Al,Fe)_8O_{15}$	Feathery euhedral crystals in V-oxide rich slag	NaV_8O_{15}	-------
$(Na,Ni)(Ca,Ni)(V,Fe,Al,Cr)_8O_{20}$	Feathery euhedral crystals in V-oxide rich slag	$NaCaV_8O_{20}$	-------
$(Fe,Ca)VO_4$ or $CaFeV_2O_7$ (?)	Bladed to feathery euhedral crystals in V-oxide rich slag	$FeVO_4$ or $CaFeV_2O_7$	-------
$(Si,Al,V)O_2$	Matrix phase & as rounded blebs in sulfide- and V-oxide rich slags	SiO_2	Obsidian
Silicates:			
$(Al,Fe)_2(Si,V,Cr,Al)O_5$	Euhedral, dismond shaped, acicular crystals in glass matrix	Al_2SiO_5	Andalusite or Sillimanite
$(Fe,Mg,Ca,Na)_2(Si,Al)O_4$	Matrix of tiny subhedral crystals intergrown w/ Pigeonite crystals	Fe_2SiO_4	Fayalite
$(Ca,Fe,Mg,Na)(Mg,Fe)(Si,Al)_2O_6$	Matrix of tiny subhedral crystals interg. w/ Fayalite crystals	$(Mg,Fe,Ca)(Mg,Fe)Si_2O_6$	Pigeonite
$(Mg,Fe)Ca_2(Si,Al)_2O_7$	Equant euhedra in glass matrix w/ spinel, sulfide, & other silicates	$MgCa_2Si_2O_7$	Åkermanite
$(Na,Ca)_4Al_3(Al,Si,V,Fe)_2Si_6O_{24}$	Euhedral, w/ spinel, glass spheres, & Fe_2O_3 in V-oxide rich slag	$(Ce,Ne)_4Al_3(Al,Si)_3Si_6O_{24}$	Sarcolite
Undeciphered silicates	Small euhedral crystals	-------	-------

Analysis of PCB's and PCDD's from the Combustion of Quicklime BInder Enhanced Densified Refuse Derived Fuel/Coal Mixtures

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Introduction

Two of the nations current major concerns are energy and municipal solid waste. The combustion of Refuse Derived Fuels (RDF) is increasingly being viewed as an attractive solution to both problems. Densification of RDF producing dRDF is typically performed to minimize the problems of handling, transporting and storing the low bulk volume material. When densification is performed with the use of a binding agent additional performance and environmental benefits can be gained.

In 1985 the University of North Texas (UNT) under contract with Argonne National Laboratory investigated over 150 potential binding agents. Evaluations were made based upon economics, toxicity, availability and performance. The top 13 binder candidates were tested in a large scale demonstration. End results found calcium hydroxide or quicklime ($Ca(OH)_2$) to be the best performing binder. UNT also hoped that this binder's basic nature might help reduce the emission of acid gases. Further conjecture was made that the binder might physically absorb halogens, such as chlorine and thus reduce the production of polychlorinated biphenyls and dioxins. (1,2)

These hypotheses were tested at a pilot plant operation at Argonne National Laboratory in 1987. The six week program combusted over five hundred tons of binder enhanced dRDF (bdRDF) blended with Kentucky coal at heat contents of 10, 20, 30 and 50 percent. The $Ca(OH)_2$ binder content ranged from 0 to 8 percent by weight of dRDF. Emission samples were taken both before and after pollution control equipment (multicyclone and spray dryer absorber). All samples were taken to UNT for analysis.

Experimental

Isokinetic samples were taken for the analysis of polychlorinated biphenyls (PCB's), polyaromatics (PAH's), polychlorinated dioxins (PCDD's) and polychlorinated furans (PCDF's). The following sampling sites were investigated.

Site 1 combustion zone (2000°F), sample site (1200°F)
Site 2 prior to pollution control equipment (300°F)
Site 3 after pollution control equipment (170°F)

Sample collection was completed using an EPA Method 5 modified sampling train, and a XAD-2 resin for trapping the majority of organics. After extractions, sample clean-up was accomplished using various acid/base modified silica and alumina gels to remove interferents. Response factors, recovery and detection limits were established through internal standards. The gas chromatography mass spectrometer analysis was performed with a Hewlett-Packard Model 5992B. (3)

Results and Discussion

The EPA's sixteen most hazardous PAH's (Table 5) and all congener groups of PCB's were tested. The results of site 2 and site 3 sampling areas are found in Tables 1 and 2. Figures 1 and 2 clearly depict a reduction in PAH and PCB emission as the binder concentration is increased. Data is not available on all compositions due to the mixing and sampling methods used. Tables 3 and 4 show the calcium and chloride contents of fly ash from the multicyclone for a series of specific compositions. The calcium is used as an indicator of the binder present in the boiler system during a particular sampling period. The increase in calcium occurring between the first coal "blank" run and the second blank occurring 3 weeks later, suggest a build-up of residual binder throughout the boiler configuration. It is noteworthy that the increase in water soluble chloride in the fly ash for the 10% RDF samples is on the same order as the reduction of PCB's seen in Figure 2. This is presumably due to the lime's ability to bind the chloride in the combustion area. The much higher chloride content of the second coal blank ash relative to the first blank can be explained by assuming a longer contact time for chloride absorption on the residual binder as the binder became saturated throughout the boiler system. (4)

The dioxin and furan analysis initially concentrated on the tetra chlorinated species present after the pollution control equipment at sample site 3. Table 6 shows that no dioxins or furans were found at the listed detection limits. Composited fly ash samples were also analysed for absorbed PCDD's and PCDF's, and again results were below detection limits. Additional analysis was performed for penta, hexa, hepta, and octa congeners at sample site

3. In all cases, no dioxins or furans were detected. These results were confirmed by collaborating with Triangle Laboratories at Research Triangle Park, NC, using their high resolution mass spectrometer. Detection limits were generally improved only on the order of one magnitude, and as before, no detectable quantities of dioxins or furans were found. (5)

Conclusion

Results of the pilot plant program indicates that the binder enhanced densified refuse derived fuel can be cofired with coal, at the levels tested, without producing detectable amounts of dioxins or furans. PCB's and PAH's are apparently reduced as a function of the quicklime binder content.

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Table 1

Polyaromatic Hydrocarbons (PAH's);

Polychlorinated Biphenyls (PCB's) at Site 2

Run#/Sample#	Site	mg PAH's cubic meter of gas sampled	mg PCB's cubic meter of gas sampled
Run 1 Sample 1	2	1.7×10^{-2}	6.2×10^{-3}
Run 2 Sample 2*	2	1.0×10^{-3}	1.3×10^{-2}
Run 2 Sample 2	2	7.6×10^{-2}	2.7×10^{-1}
Run 3 Sample 1	2	1.6×10^{-2}	1.4×10^{-2}
Run 4 Sample 1	2	4.0×10^{-3}	7.6×10^{-3}
Run 4 Sample 2	2	8.1×10^{-3}	7.7 xx 10^{-3}
Run 5 Sample 1	2	3.5×10^{-2}	9.7×10^{-3}
Run 5 Sample 2	2	4.6×10^{-2}	7.7×10^{-3}
Run 7 Sample 1	2	2.2×10^{-1}	2.0×10^{-3}
Run 7 Sample 2	2	3.5×10^{-1}	2.9×10^{-1}
Run 8 Sample 2	2	2.4×10^{-1}	1.3×10^{-2}
Run 8 Sample 4	2	3.0×10^{-1}	3.4×10^{-3}
Run 12 Sample 1	1	3.4×10^{-1}	5.4×10^{-3}
Run 12 Sample 2	2	1.3×10^{-1}	3.9×10^{-4}

* This sample was lighter in color than all the rest

Table 2

Polyaromatic Hydrocarbons (PAH's);

Polychlorinated Biphenyls (PCB's) at Site 3

Run#/Sample#	Site	mg PAH's cubic meter of gas sampled	mg PCB's cubic meter of gas sampled
Run 1 Sample 1	3	4.6×10^{-3}	5.3×10^{-4}
Run 2 Sample 1	3	6.3×10^{-3}	1.2×10^{-3}
Run 2 Sample 2	3	1.5×10^{-2}	*
Run 2 Sample 3	3	8.1×10^{-3}	1.6×10^{-3}
Run 3 Sample 1	3	7.3×10^{-3}	9.1×10^{-3}n
Run 4 Sample 1	3	7.3×10^{-3}	1.1 xx 10^{-4}
Run 4 Sample 2	3	3.1×10^{-3}	3.1×10^{-3}
Run 5 Sample 1	3	3.6×10^{-4}	2.8×10^{-4}
Run 5 Sample 2	3	4.0×10^{-3}	1.2×10^{-3}
Run 7 Sample 1	2	7.9×10^{-2}	4.2 xx 10^{-2}
Run 7 Sample 2	3	4.9×10^{-2}	6.5×10^{-3}
Run 8 Sample 1	3	1.0×10^{-3}	2.4×10^{-3}
Run 8 Sample 2	3	8.1×10^{-3}	8.5×10^{-4}
Run 12 Sample 1	3	7.0×10^{-2}	4.0×10^{-3}
Run 12 Sample 2	3	1.4×10^{-3}	4.3×10^{-4}

* Interference made it impossible to determine the quantity of PCB's in this run

Table 3

Calcium Levels in Fly Ash

Fuel	ppm of Calcium
First coal blank	3,000
Coal - 10% dRDF (0% binder)	6,700
Coal - 10% dRDF (4% binder)	10,600
Coal - 10% dRDF (8% binder)	15,000
Second coal blank	4,200

Table 4

Inorganic Chloride Levels in Fly Ash

Fuel	ppm of Chloride
First coal blank	100
Coal - 10% dRDF (0% binder)	190
Coal - 10% dRDF (4% binder)	280
Coal - 10% dRDF (8% binder)	320
Second coal blank	280

Table 5

EPA Priority PAH's

Napthalene	Benzo-a-anthracene
Acenapthylene	Chrysene
Acenapthene	Benzo-b-fluoranthene
Flourene	Benzo-k-fluoranthene
Phenanthrene	Benzo-a-pyrene
Anthracene	Dibenzo-a,h-anthracene
Fluoranthene	Benzo-g,h,i-perylene
Pyrene	Idendo-1,2,3,-g,d-pyrene

Table 6

Tetra-Chlorinated Dioxins and Tetra-Chlorinated Furans at Site 3

Run#/Sample#	Site	Tetra-Chlorinated Dioxin Level	Tetra-Chlorinated Furan Level	Detection Limit
Run 1 Sample 1	3	BDL	BDL	0.72 ng/m^3
Run 2 Sample 1	3	BDL	BDL	1.99 ng/m^3
Run 2 Sample 2	3	BDL	BDL	4.07 ng/m^3
Run 2 Sample 3	3	BDL	BDL	5.24 ng/m^3
Run 3 Sample 1	3	BDL	BDL	4.80 ng/m^3
Run 4 Sample 1	3	BDL	BDL	4.27 ng/m^3
Run 4 Sample 2	3	BDL	BDL	4.27 ng/m^3
Run 5 Sample 1	3	BDL	BDL	0.49 ng/m^3
Run 5 Sample 2	3	BDL	BDL	0.47 ng/m^3
Run 7 Sample 1	3	BDL	BDL	4.16 ng/m^3
Run 7 Sample 2	3	BDL	BDL	4.10 ng/m^3
Run 8 Sample 1	3	BDL	BDL	4.78 ng/m^3
Run 8 Sample 2	3	BDL	BDL	4.78 ng/m^3
Run 12 Sample 1	3	BDL	BDL	3.85 ng/m^3
Run 12 Sample 2	3	BDL	BDL	4.85 ng/m^3

ng/m^3 = nanograms per cubic meter

BDL = Below Detection Limits

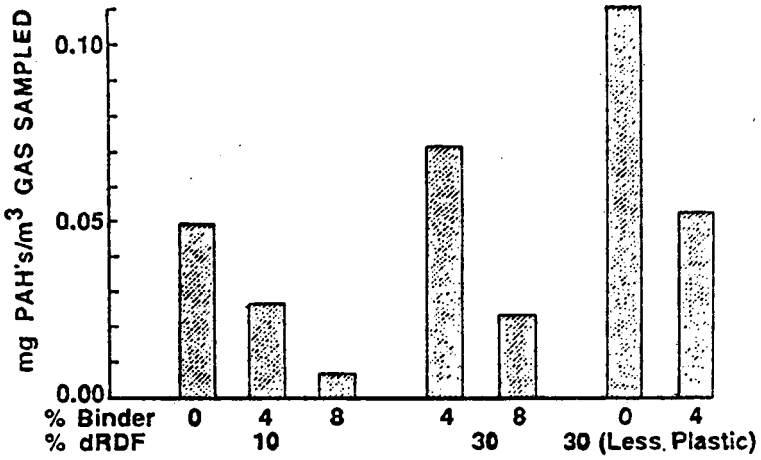

Figure 1

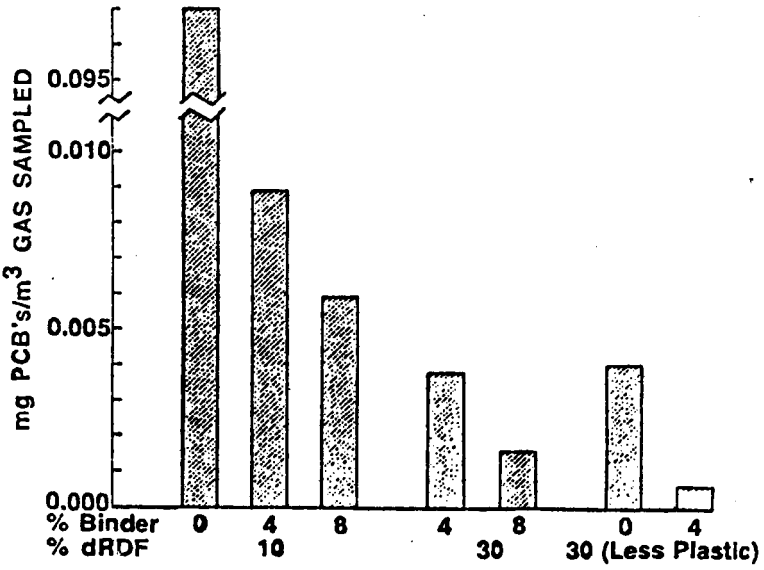

Figure 2

A METHODOLOGY FOR ASSESSING THE FEASIBILITY OF DEVELOPING AND TRANSFERRING NEW ENERGY TECHNOLOGY TO THE MARKETPLACE. Dr. H. M. Kosstrin and Dr. B. E. Levie, R. W. Beck and Associates, 1125 17th Street, Suite 1900, Denver, Colorado 80202.

Any new process intended to produce clean energy from waste should be characterized for its ultimate feasibility of becoming commercially successful. A four-phase strategy to analyze the process and plan for scaleup is presented. First, the new technology is assessed in terms of its market potential based on laboratory, bench scale or pilot data. A comparison with competing commercial technology is performed to compare the technology with its competition by estimations of factors such as life cycle cost, public acceptance, and adaptability to changing conditions and fuels. Second, the current status is reviewed with respect to theory, laboratory or pilot scale results, and available cost data. Third, the path to commercialization is outlined. The stages of scaleup and data required to prove the concept and remove risks of commercialization are identified. Finally, the financing needs for the various stages of scaleup and for a commercial unit are determined.

Introduction

Development of any new technology has traditionally been a controversial subject due to high expectations shared by proponents and results which many times fall short of these expectations. Solid and liquid waste management has seen both success and failure in the implementation of new technology. For example, promises to commercially produce liquid or gaseous fuels and/or chemicals from municipal solid waste (MSW) or refuse derived fuel (RDF) have so far been unfulfilled after several attempts at demonstrating various technologies. These failures encourage us to examine new and undeveloped technology in a more sophisticated and step-wise manner than has been previously done. By learning from past failures and taking a methodical and proactive approach to scaling-up suitable technology, we can better direct development so that realistic expectations can be made and met. The approach discussed here will increase chances for successful development of new waste management technologies.

The following phases outline the approach to be presented:

I. Determine if a technology at its current state of development, either conceptual, bench, or pilot scale can be potentially competitive with commercial technologies today.

II. Establish the current status of the technology and what needs to be better understood before progressing.

III. Establish the path which would most logically be taken to result in commercializing the technology.

IV. Identify the requirements of different financing options necessary to commercialize the technology.

These phases follow a progression in which the results of each builds on the results from the preceding phases. This review can be started at any time in the development process and should be updated to account for new data on the technology, the competition, or the market as they become available.

Review and analysis of new technology can be biased according to the perspective of the reviewer. The investigators, developers, and sponsors all have vested interests in the technology which may prevent a balanced view of the technology, its development, or its commercialization. Investors and lenders typically look for independent reviews of the technology prior to committing large amounts of capital. This can best be accomplished by persons without conflicts of interest and with an adequate background reviewing development of the technology.

Review of the Concept

In this initial stage of analysis, the technology is looked at objectively to assess its niche in current markets. The first step is to identify the market or markets where the technology would most likely be competing and to broadly establish a range of competitive pricing for the service provided or product produced. It is important to consider all areas where the technology could potentially compete, including those outside the primary field of interest. High value chemicals, resins, and plastics, for instance, may be more economically feasible to produce than fuels from certain feedstocks.

Questions to resolve before proceeding are those which would be important to an investor. These generally will establish if the market is potentially strong and lasting. In the area of solid waste management, the following questions can be used as guidelines to ascertain the market's potential. Similar questions can be developed for any particular field.

- Is market expanding?
- Is it monpolistic or controlled by a few companies?
- What are the minimum or maximum requirements for waste needed to be processed?
- Is the waste composition changing due to recycling, composting, changes in consumption, etc.?
- Are markets localized, where are they located?
- Do long-term contracts either for feedstocks or products already exist which would interfere with this technology?
- What are the standards for the product produced?
- Can environmental permits be obtained?
- What are the characteristics of markets for byproducts of the process?

The next step in reviewing a new technology is to compare the technology with those commercial technologies currently in the identified market(s). This comparison can be as brief or extensive as is desired, depending on if we are considering a revolutionary change or just an evolutionary advance in the market. At a minimum, cost and environmental comparison should be made between the new technology and what is available in the market. The cost should be assessed on a life-cycle basis, accounting for capital, operation and maintenance, disposal of residue costs, and revenues from tipping fees, the primary product and any byproducts. The general environmental assessment could include a number of considerations including impacts on air, water, workers, noise, and flora and fauna.

There are many other considerations in performing this initial assessment. The feedstock must be compatible with the technology, and the product(s) compatible with the existing markets. Flexibility can be quite advantageous in the waste management industry, as the quantities and composition of waste is rarely fixed. While some technologies might only be competitive for a certain type and quantity of waste, others could take many types of waste, in a range of quantities. Effects on other related technologies should be assessed, as today municipalities and other organizations are interested in integrated solid waste management. Generally no one technology can solve the waste problems for a given location. Thus, technologies which can work effectively together may be more desirable than those which prevent other technologies and strategies from being employed successfully.

In order to compare the new technology with existing ones, it must be emphasized that the new technology should be judged on a realistic basis. A conservative estimate for costs, revenues and efficiency of the new process should be used for comparison purposes. Often a new technology assessment under estimates commercialization costs and greatly over estimates potential revenues from products.

Establishing Current Status of the Technology

The second phase of this review is to establish the current status of the new technology, providing a baseline or framework from which further development can be compared. The initial limited economic feasibility developed in Phase I, can be updated with new information gained in this phase. Technical and economic gaps in knowledge should be identified in this phase and either resolved now or targeted for later development work and/or analysis.

Existing Data Review

This stage of review is many times performed by the researchers in order to propose further expenditures or justify previous funding. Therefore, some data may already exist for this analysis.

The first part of establishing the current status is to verify that the process proposed is physically possible and practically attainable. This will require checking previous assumptions, reviewing theory and obtaining

correct parameter values for thermodynamic, kinetic and mass and heat transfer. Mass and energy balances should be done to check process feasibility. A second law analysis could be performed on the process to identify inefficiencies.

Once the theory has been reviewed, operational data from the lab, bench, and/or pilot facility should be assessed to determine the deviation from theory. This will allow a better estimate of expected yields as the process is scaled-up further. It will also serve to highlight areas where the process can be improved or is not performing as well as expected. In some cases, it will point to the fact that the data is inaccurate or insufficient for reasonable analysis and that additional and more accurate data must be obtained before further progress can be made. It is important in this review that sufficient data be available to determine the precision of the data. Furthermore, there should be an adequate review of the instrumentation and data acquisition system to determine any measurement biases which exist. For example, biases occur in high temperature measurements, and when measurements are made close to the detection limit of the instrumentation.

Once a thorough review of the available data has been accomplished, we need to update our original economic model. Existing cost data should be reviewed to better establish costs of the technology at its present state of development. These costs should be segregated as much as possible into standard technologies and developmental technologies to identify which areas need more accurate estimates as development proceeds. If possible, costs for each piece of equipment or unit operation should be tabulated.

Many costs will not be available based on pilot plant data, such as upstream and downstream equipment which may not be implemented at this stage of development. But this equipment can be estimated if standard technology is used. Equipment in this category may include material waste recovery systems, gas cleaning, liquid cleaning, heat recovery equipment, and emissions, effluent and residue treatment systems.

Costs for operation and maintenance (O&M) are difficult to determine as pilot scale or smaller equipment will rarely run for long continuous periods of time. Some costs may be determined such as on energy requirements, energy losses, and other requirements of the process such as gases, water, or other utilities. Costs associated with running the process for long periods of time will generally not be available. But preliminary estimates can be made, and ranges input to the economic model to establish a current economic status.

Technical and Economic Questions

The review of the current status will raise various questions on both a technical and cost basis. Technical questions which are easily resolved with current equipment should be addressed as soon as possible prior to going on to Phase III.

It is generally far less expensive to acquire data at the initial stages of development than later on, and this data can provide many benefits. The additional data taken may indicate unusual phenomena occurring which need to be understood for successful scale-up. Extra information may point to flaws in the technology such as larger heats of reaction than calculated, poor kinetic rates, or poor catalytic activity. Such results might be indicated using extra thermocouples, calorimetry, gravimetric monitoring, etc. These may be economical to measure at this stage of development, but not once the technology is scaled-up. Discrepancies between actual operating data and theoretical projections may indicate poorly understood phenomena, inaccurate data, or invalid assumptions in the theory. These technical data gaps may need to be filled before further progress should be attempted.

Technical questions which may be unanswerable include environmental impacts, reliability of equipment over time, labor necessary to run and maintain operations full time, and degradation of process over time due to unknown phenomena. These questions will need to be revisited in later phases of development, and should be noted to trigger later activity.

Economic questions which may not yet be answered should be identified at this point and noted for later resolution. These may include questions of costs for upgrading the products and byproducts for sale, prices for the products and byproducts, and disposal costs for residues and effluents. Some of these questions are best left for later stages in development, when more representative products and residues will be produced. By initially establishing costs of upgrading or treating products or residues, it may be revealed that further consideration needs to be given to different methods of treatment. This may need to be worked on before, or concurrent to scaling-up.

Establishing a Path to Commercialization

Now that the current status of the emerging technology has been established and we have updated the economic model with new information, which still projects a competitive product, we can establish how to proceed. This third phase of development can consume fairly large amounts of capital, so a critical assessment should be conducted to establish a deliberate agenda so that an investor may be convinced to fund this phase.

The initial task of this phase is a risk assessment to identify any technical flaws in the concept, and establish a plan to address and overcome any obstacles. As an example, the process data from bench scale operations has confirmed the kinetic viability of the process but has left unanswered certain mechanical questions. For instance, we know the reactor works but we have assumed in our model a feeder that can use unprocessed feedstock. The problem identified is, how do we introduce the solid feedstock in a uniform, continuous manner without excessive preprocessing. This risk assessment, which should include all components, is intended to identify components of the process that either require further development prior to proceeding to the first scale-up or to find an acceptable alternative.

The final piece of the risk assessment is to critically look at the question of scale-up. One may ask the question, how far can we proceed, in this initial step from bench scale? But the right question is, what is the maximum scale-up possible from the final development unit to the commercial demonstration? Answering this question is a key to determining the total path to commercialization. We can then decide on how many scale-up steps to take and when critical components should be scaled-up. These steps may include any or all of the following: an integrated pilot plant, a semi-works to prove out critical components or a complete demonstration system.

After planning the global technical approach, and the required component development has been identified, we need to feed any revisions to our overall cost model to reconfirm feasibility. The next stage is to determine the additional technical data, whether mechanical or process, that is required.

Typical questions which help identify such data include:

- Does each component work as intended?
- Does the system as a whole work together in a safe manner?
- Does proper selection of materials take into consideration "corrosive and errosive elements in the process and can I maintain product specifications?

In addition, the duration of acquiring the answers to these questions should be established. Typical goals of this first scale-up may be 5,000 hours of total test time with perhaps 1,000 hours of continuous operation under design conditions. The purpose of this scale-up is to work through the operational and process problems, confirm yields and product quality, and obtain an indication of reliability. The "other" objective is to be able to again refine the economic model with the data obtained from this first scale-up for both capital and operations costs. We will need this information, since we are approaching the time that additional capital will be needed for the next scale-up or for a continuously operational demonstration facility.

Once we have established technically what type of data and scaled-up system the technology requires, we need to establish a cost of this phase of the work and raise additional capital. At this stage, it is important to consider if any revenue can be derived from the operation of the development unit to offset the operational costs. This may not be realistic, but an investor typically likes to see some "pay as you go" operation while development is progressing.

After the development unit has completed the technical data acquisition, it is again time to refine our feasibility model with new cost data, operational data and reliability data. The level of success of the

development unit will at times determine the type of financing that the process developer can consider. The final section discusses the various options.

The First Commercial Unit - How Can It Be Financed

As we complete Phase III, the additional data collected from the scaled-up operation is again fed back into the economic model to reconfirm feasibility. A positive result will now enable the project to proceed to raise the capital necessary to build a full scale facility which, by definition, when successful will be the first commercial unit.

Financing can be obtained from a variety of sources, ranging from total equity, where the investor assumes all the risk, to non-recourse project financing where the risk of failure is divided between the lender and the equity participant. Technologies concerned with the disposal or processing of solid waste are currently eligible to obtain tax exempt bonding authority. The lower cost of capital by using tax exempt bonds is a commonly used method to enhance the overall economics of a project.

Funding a new technology using non-recourse project financing, typically requires either some level of equity participation or a guarantee to pay back the debt, or some combination of the two. The level of equity participation or debt guarantee depends on the characteristics of the project and the projected economics as determined by an Independent Engineering Study. This Independent Engineering Review is critical to both lenders and equity participants, since it is intended to confirm both the technical and economic viability of the technology.

From a lender's point of view, the typical characteristics of a strong project include some or all of the following:

- A turnkey construction contract including a fixed price, fixed completion date, detailed performance test and penalties for nonperformance.
- An operations and maintenance contract with a fixed price and incentives for positive performance and penalties for poor performance.
- Independent projections based on the technology and contract structure which show adequate cash flow to cover all expenses and debt service. These projections should be done for both the expected operational scenarios and in cases where potential problems may arise that are either technical or economical in nature.

Raising the capital for a new technology can be as challenging as completing the technical development. However, this job is easier when the proper groundwork has been laid by following the methodology presented here.